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(54) VINYLIC RESIN COMPOSITION.

(57) This invention discloses a vinyllic resin composition comprising a polyamide-imide elastomer resin composition and optionally containing an electrolyte added thereto, wherein the elastomer resin composition is prepared by the reaction among a vinyllic polymer, a mixture comprising caprolactam, an aromatic polycarboxylic acid and a specified polyoxyethylene glycol, and 0 to 0.5 mole, per mole of the glycol in the mixture, of a diamine etc., and has a glycol content of 85 to 30 % by weight and a relative viscosity of at least 1.5 at 30 °C. The invention also discloses a product of molding of said composition.

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THE POLYMER  
see front page

## SPECIFICATION

## TITLE OF THE INVENTION

## VINYL RESIN COMPOSITION

## 1 TECHNICAL FIELD

The present invention relates to resin compositions which contain a vinyl resin such as a styrene resin or an acrylic resin, and a polyamideimide elastomer. In particular, said resin compositions have an excellent permanent antistatic property and those having a styrene resin base can be used as antistatic materials for various parts of electronic devices, household appliances, office automation equipment, etc., including video cassettes and video disks. Those having an acrylic resin base also have an excellent permanent antistatic property and good transparency. They are inexpensive, and can be used as antistatic materials for various parts of electronic devices, household appliances, office automation equipment, etc., including, for example, lighting fixtures, instrument nameplates and meter covers.

## BACKGROUND ART

Styrene resins are inexpensive and excellent in mechanical properties such as mechanical strength and rigidity and in moldability, and accordingly, they are widely used in a variety of fields. However, styrene

1 resins are likely to cause problems due to the  
development of electrostatic charge when they are used  
in parts of electronic or electric equipment such as  
video cassettes, IC cards, copying machines, televisions  
5 etc., or to cause a staining problem by sticking of the  
dust caused by electrostatic charges when used in  
housings of household appliances, office automation  
equipment, etc.

On the other hand, acrylic resins are  
10 excellent in transparency and rigidity and hence are in  
wide use as the material of various parts of electronic  
devices, household appliances, office automation  
equipment, etc., including, for example, lighting  
fixtures, instrument nameplates and meter covers.

15 However, similarly to styrene resins, acrylic  
resins have a high specific surface resistance and are  
readily electrified by friction etc., so that they are  
likely to present a poor appearance due to the sticking  
of the dust and dirt, or cause problems due to the  
20 development of electrostatic charge when they are used  
in parts of electronic instruments or the like.

Accordingly, there has been a desire for the  
development of a material based on vinyl resins, such as  
styrene resin and acrylic resin, which has been imparted  
25 good antistatic property, while retaining the excellent  
characteristic properties which are inherent to these  
resins.

1           As to the method for imparting an antistatic  
property to said vinyl resins, it is well known, for  
example, to incorporate a surface active agent into the  
resin or coating the agent on the resin surface. In  
5 such methods, however, the antistatic agent present on  
the surface is likely to be removed by water-washing,  
rubbing, etc., and to impart a permanent antistatic  
property to a surface is difficult.

          Methods comprising adding a polyamide  
10 elastomer to a styrene resin to improve the impact  
resistance and antistatic property of the styrene resin  
have been proposed in Japanese Patent Application Kokai  
Nos. 59-193,959, 60-23,435, 63-95,251 and 63-97,653,  
etc.

15           The polyamide elastomers used in the above  
methods include a polyetheresteramide wherein the hard  
segment is polyamide, the soft segment is polyether and  
the two segments are connected by an ester linkage; a  
polyetheramide wherein said two segments are connected  
20 by an amide linkage; and a polyesteramide wherein the  
soft segment is polyester. However, the compatibility  
of these polyamide elastomers with styrene resins is  
poor.

          Japanese Patent Application Kokai No. 59-  
25 193,959 discloses the use of a vinyl copolymer, obtained  
by copolymerizing a vinyl monomer containing a carboxyl  
group, to improve the compatibility thereof with a  
polyamide elastomer and to improve the impact resistance

1 of the composition formed. However, since 40% by weight  
or more of a polyamide elastomer is used in this case,  
the resulting composition has a decreased rigidity.

Japanese Patent Application Kokai No. 60-

5 23,435 discloses a composition comprising 5-80 parts by  
weight of a polyetheresteramide and 95-20 parts by  
weight of a vinyl copolymer containing a carboxyl group.  
Although the composition is improved in compatibility  
and antistatic property, a large amount of the  
10 polyetheresteramide must be added in order to obtain a  
practically useful antistatic property, which resulted in  
the flexural modulus being unsatisfactory.

Japanese Patent Application Kokai No. 63-

15 95,251 discloses a composition comprising a polyether-  
esteramide, a rubber-modified styrene resin and a vinyl  
copolymer containing a carboxyl group, which gives  
molded products having good antistatic property and  
gloss.

Further, Japanese Patent Application Kokai No.

20 63-97,653 discloses a composition obtained by finely  
dispersing a polyamide elastomer having a size of 0.01 -  
10  $\mu\text{m}$  into a styrene resin to eliminate laminar peeling  
and to impart an antistatic property.

Polyamide elastomers hitherto investigated for  
25 incorporation into styrene resins are polyetherester-  
amides, polyetheramides, and polyesteramides. However,  
polyetheramides are disadvantageous with regard to cost  
because the process for the production of polyether-

1 diamines is complicated and expensive when polyether-  
diamines are used. Polyesteramides have a low  
hydrophilicity and exhibit an antistatic effect with  
difficulty.

5           Among these, polyetheresteramides are  
advantageous with regard to cost since they can be  
obtained from relatively inexpensive polyoxyalkylene  
glycols, as the raw material. Accordingly, an attempt  
has been made to use them and to improve also the  
10 flexural modulus (Japanese Patent Application Kokai No.  
63-95,251). However, polyetheresteramides are not fully  
satisfactory in thermal resistance and, when blended  
into styrene resins and exposed to high temperatures for  
a long period of time in molding operations, etc., the  
15 resulting molded products would sometimes undergo  
deterioration in properties including mechanical  
properties and antistatic property.

On the hand, with regard to the methods for  
imparting a permanent antistatic property to acrylic  
20 resins, there have been disclosed, for example, (1) a  
method comprising blending into acrylic resins, a vinyl  
copolymer having a polyoxyethylene chain and a structure  
of sulfonic acid salt, carboxylic acid salt or  
quaternary ammonium salt (Japanese Patent Application  
25 Kokai Nos. 55-36,237 and 63-63,739) and (2) a method  
comprising blending a polyetheresteramide into methyl  
methacrylate-butadiene-styrene copolymers (i.e., MBS  
resin) or methyl methacrylate-acrylonitrile-butadiene-

1 styrene copolymers (i.e., MABS resin) (Japanese Patent Application Kokai No. 62-119,256).

In method (1) mentioned above, however, the vinyl copolymer to be blended uses a special vinyl  
5 monomer and hence is expensive, so that the production cost of the acrylic resin blended with said copolymer becomes inevitably high. Moreover, in the method described in Japanese Patent Application Kokai No. 55-36,237, the amount of the vinyl copolymer blended is  
10 large and the deterioration of thermal resistance, etc., which is inherent in an acrylic resin, cannot be avoided. On the other hand, in method (2) mentioned above, the amorphous polyetheresteramide and the MBS or MABS resins are so selected that the difference in their  
15 refractive indices is 0.02 or less to ensure the transparency of the resulting composition. This restricts the degree of freedom of the combination and in the case of polymethyl methacrylate, a typical acrylic resin, the refractive index can be difficultly  
20 adapted, resulting in lowered transparency.

A prominent feature of acrylic resins is their excellent transparency. When a polymer is blended into acrylic resin to impart a permanent antistatic property thereto, however, the polymer is frequently poor in  
25 compatibility with the acrylic resin, resulting in a product of lowered transparency; or even when a product of good transparency is obtained, the product shows an insufficient antistatic effect or a decreased thermal

1 resistance. Further, when a polymer of a complicated  
structure is prepared to obtain a satisfactory  
antistatic effect it leads to a high production cost,  
and an acrylic resin which is inexpensive and has a good  
5 antistatic property cannot be obtained.

#### DISCLOSURE OF THE INVENTION

The object of the present invention is to  
provide vinyl resin compositions having a permanent  
antistatic property overcoming the above-mentioned  
10 difficulties. The compositions include a styrene resin  
composition which has a high rigidity and sufficient  
thermal resistance and exhibits a practical and useful  
antistatic property, and an acrylic resin which has an  
excellent antistatic property, thermal resistance and  
15 transparency.

The present inventors have made an extensive  
study on the blend of vinyl resins with a thermoplastic  
elastomer comprising polyoxyethylene glycol as the  
principal soft segment, to attain the above-mentioned  
20 object. As a result, it has been found that a  
polyamideimide elastomer comprising polyoxyethylene  
glycol as the soft segment and a polyamideimidedi-  
carboxylic acid obtained from caprolactam and a tribasic  
or tetrabasic aromatic polycarboxylic acid capable of  
25 forming at least one imide ring, such as trimellitic  
acid or pyromellitic acid, as the hard segment has a  
good compatibility with vinyl resins and a good thermal



1 resistance, and can exhibit an excellent antistatic  
effect, even when present in a relatively small amount.

Further, it has been found that the thermal  
resistance and the melting point of said polyamideimide  
5 elastomer depend mainly on the proportion and the  
molecular weight of the hard segment, that an elastomer  
obtained by using a polyamideimide-dicarboxylic acid  
partly modified with a diamine or diisocyanate also has  
a good affinity for vinyl resins and a good thermal  
10 resistance, that said elastomer gives vinyl resin  
compositions of a satisfactory rigidity and, when  
combined with acrylic resins, yields transparent  
compositions, and that the antistatic property of said  
composition can be further improved by incorporating  
15 therein a specific proportion of a specified compound.  
The present invention has been accomplished on the basis  
of above findings.

Thus, the present invention provides a vinyl  
resin composition which comprises 100 parts by weight of  
20 a resin composition comprising

- (A) 97 - 70% by weight of a vinyl polymer and
- (B) 3 - 30% by weight of a polyamideimide  
elastomer obtained from

- a) caprolactam,
- 25 b) a tribasic or tetrabasic aromatic  
polycarboxylic acid capable of forming at least one  
imide ring,

1           c) polyoxyethylene glycol or a mixture of at least 50% by weight of polyoxyethylene glycol and a polyoxyalkylene glycol other than polyoxyethylene glycol, and

5           d) 0 - 0.5 mole of a diamine or diisocyanate compound per 1 mole of the glycol of the component c), the glycol component c) being present in a proportion of 85 - 30% by weight in the elastomer and the relative viscosity of said elastomer being at least 1.5 at a  
10 temperature of 30°C, and

(C) 0 - 10 parts by weight of at least one electrolyte selected from organic electrolytes or inorganic electrolytes.

#### BEST MODE FOR CARRYING OUT THE INVENTION

15           The present invention will be described in detail below.

          The vinyl resins (A) used in the present invention include styrene resins and acrylic resins. As examples of styrene resins, mention may be made of  
20 rubber-modified polystyrene resin, styrene-butadiene-acrylonitrile copolymer (ABS resin), styrene-rubber copolymer-methyl acrylate or -methyl methacrylate (MBS resin), styrene-acrylonitrile copolymer (AS resin), and random, block or graft polymer obtained from styrene  
25 monomer as the main component and copolymerizing therewith another vinyl monomer, such as methyl

1 methacrylate, methyl acrylate, maleimide, acrylamide,  
etc.

Further, there may be used styrene resins  
incorporated with other thermoplastic resins, for  
5 example, blends of rubber-reinforced styrene resin with  
styrene-butadiene copolymer or hydrogenated styrene-  
butadiene copolymer, polyblends of ABS resin with  
polycarbonate resin, polyblends of ABS resin with  
acrylic resin, and polyblends of ABS resin with vinyl  
10 chloride resin.

Said rubber-reinforced polystyrene resin used  
in the present invention is produced, commercially, by  
dissolving a rubber-like substance in styrene monomer  
and subjecting the resulting solution to bulk or  
15 suspension polymerization. The rubber-like substances  
used are polybutadiene, styrenebutadiene copolymer, and  
the like. They are usually dispersed in styrene resin  
as particles of an average particle diameter of 0.5 -  
5  $\mu\text{m}$ .

20 Further, resins obtained by substituting a  
part of the styrene units constituting the above-  
mentioned styrene resins with  $\alpha$ -methylstyrene, p-  
methylstyrene and p-t-butylstyrene units or such which  
may also be used.

25 Styrene resins containing carboxyl, epoxy,  
oxazoline, amide, imide, hydroxyl, amino, and the like,  
may also be favorably used to improve their affinity for  
polyamideimide elastomers. There is no particular

1 restriction as to the method for introducing these  
functional groups into styrene resins. It may be  
performed by adding a monomer having a functional group  
and capable of copolymerizing with styrene monomer, for  
5 example, acrylic acid, methacrylic acid, fumaric acid,  
maleic acid, 2-hydroxyethyl methacrylate, 2-hydroxyethyl  
acrylate, 3-hydroxypropyl methacrylate, maleic  
anhydride, itaconic anhydride, chloromaleic anhydride,  
2-isopropylaminoethylstyrene, aminoethyl acrylate,  
10 aminopropyl methacrylate, vinyloxazoline, glycidyl  
methacrylate, glycidyl acrylate, etc. and copolymerizing  
at the time of polymerization of the above-mentioned  
styrene resins, or by blending the copolymerization  
products of these monomers with styrene into said  
15 styrene resins.

Though it is not definitely clear through what  
mechanism the antistatic effect is exhibited when these  
functional group-containing styrene resins are blended  
with polyamideimide elastomer. It has been found that  
20 such blends undergo no laminar peeling, show an  
appropriate degree of compatibility not reaching  
complete mutual solubility between the two components,  
and express excellent antistatic effect and mechanical  
properties.

25 The content of the functional groups contained  
in said functional group-containing styrene resins is  
selected in the range of 0.05 - 10% by weight, preferably  
0.1 - 5% by weight. When the content is less than

1 0.05% by weight the effect of improving mechanical  
properties cannot be exhibited sufficiently, whereas  
when it exceeds 10% by weight the antistatic effect is  
lowered.

5           The carboxyl group exerts a particularly  
strong action toward improving compatibility. The  
content of carboxyl groups in the styrene resin is  
preferably 0.05 - 4% by weight, more preferably 0.1 - 2%  
by weight. When the carboxyl group content is less than  
10 0.05% by weight, the affinity of the resin for  
elastomers with a high polyamideimide content,  
particularly elastomers containing 60% by weight or more  
of polyamideimide decreases, leading to a decrease in  
impact resistance and a decrease in elongation. On the  
15 other hand, when the content is higher than 4% by  
weight, the affinity for polyamideimide elastomer  
increases, resulting in an extremely fine dispersion of  
the elastomer, and the blend approaches a state of  
complete mutual dissolution. Resin blends in such a  
20 condition exhibit an antistatic effect with difficulty.

Acrylic resins which may be used as component  
(A) in the present invention are, for example,  
polymethyl methacrylate (MMA resin), rubber-reinforced  
polymethyl methacrylate, methyl methacrylate-butadiene-  
25 styrene copolymer (MBS resin), methyl methacrylate-  
acrylonitrile-butadiene-styrene copolymer (MABS resin),  
and polymers obtained by copolymerizing 60% by weight or  
more of methyl methacrylate and 40% or less of another

1 copolymerizable vinyl monomer. These resins may be used  
alone or in combinations of two or more. Examples of  
said copolymerizable vinyl monomer include ethyl  
methacrylate, butyl methacrylate, cyclohexyl  
5 methacrylate, 2-ethylhexyl methacrylate, methyl  
acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl  
acrylate, styrene,  $\alpha$ -methylstyrene, acrylonitrile,  
acrylic acid, methacrylic acid, fumaric acid, maleic  
acid and itaconic acid.

10 The polyamideimide elastomer of component (B)  
of the present composition is a multi-block type  
copolymer obtainable from a mixture of (a) caprolactam,  
(b) a tribasic or tetrabasic polycarboxylic acid, (c)  
polyoxyethylene glycol or a polyoxyalkylene glycol  
15 comprising polyoxyethylene glycol as the main component  
and optionally (d) a diamine or a diisocyanate,  
polyamideimide constituting the hard segment being  
formed of components (a), (b) and (d) and said hard  
segments being connected through an ester linkage to the  
20 glycol of the component (c) constituting the soft  
segment.

As component (b), there are used tribasic or  
tetrabasic aromatic carboxylic acids capable of forming  
at least one imide ring through a reaction with amino  
25 group(s) or the anhydrides thereof.

Specific examples of tricarboxylic  
acids include 1,2,4-trimellitic acid, 1,2,5-naphthalene-  
tricarboxylic acid, 2,6,7-naphthalenetricarboxylic acid,

1 3,3',4-diphenyltricarboxylic acid, benzophenone-3,3',4-tricarboxylic acid, diphenyl sulfone-3,3',4-tricarboxylic acid, and diphenyl ether-3,3',4-tricarboxylic acid.

5                    Specific examples of                    tetra-carboxylic acids include pyromellitic acid, diphenyl-2,2',3,3'-tetracarboxylic acid, benzophenone-2,2',3,3'-tetracarboxylic acid, and diphenyl ether-2,2'-3,3'-tetracarboxylic acid.

10                   These polycarboxylic acids are used in a substantially equimolar amount, namely in the range of 0.9 - 1.1 times by mole, relative to the sum of glycol component (c) and diamine or diisocyanate component (d).

                  Examples of the diamines or diisocyanates used  
15 as component (d) include ethylenediamine, tetramethylenediamine, hexamethylenediamine, phenylenediamine, 4,4'-diphenylmethanediamine, hexamethylene diisocyanate, phenylene diisocyanate, tolylene diisocyanate and diphenylmethane diisocyanate. The  
20 introduction of these makes it possible to increase the number of imide rings in the hard segments and thereby improve the thermal resistance, lower the melting point by copolymerization and control the thermal stability in kneading and the flow characteristics in kneading and  
25 molding. The amount of the diamine or diisocyanate of component (d) to be used should be 0.5 mole or less relative to 1 mole of glycol component (c). When the amount is larger than said value, a homogeneous

1 elastomer can be difficultly obtained and the  
compatibility with vinyl resins becomes low.

Polyamideimide of the hard segment is related  
to the thermal resistance, strength and hardness of the  
5 elastomer and compatibility with vinyl resins. The  
content of polyamideimide in the elastomer should be in  
the range of 15 - 70% by weight. When the content is  
less than 15% by weight the elastomer has a low  
strength, and gives a product of low impact strength  
10 when blended with vinyl resin. A content exceeding 70%  
by weight results in poor compatibility or low  
antistatic effect.

The effect of said hard segment content is  
particularly large in the case of an acrylic resin. For  
15 example, to maintain the transparency of MMA resin when  
blended with said elastomer, the content of the hard  
segment is preferably 35% by weight or less.

The number average molecular weight of  
polyamideimide is preferably not less than 500 and not  
20 more than 3,000, more preferably not less than 500 and  
not more than 2,000. When the number average molecular  
weight of polyamideimide is less than 500 the melting  
point is lowered and the thermal resistance is  
decreased, whereas when it exceeds 3,000 compatibility  
25 with vinyl resins is lowered.

The components (c) used in the polyamideimide  
elastomer are polyoxyethylene glycol or mixtures of



1 polyoxyethylene glycol with polyoxyalkylene glycols  
other than polyoxyethylene glycol.

The number average molecular weight of  
polyoxyethylene glycol used is not critical, but  
5 preferably in the range of 500 - 5,000. When it is less  
than 500, it may lead to a low melting point and as a  
result to an insufficient thermal resistance, although  
also depending on the composition of the elastomer.  
When it exceeds 5,000 a tough elastomer is formed with  
10 difficulty, which may result in low impact strength and  
low rigidity of the product when the elastomer is  
blended with vinyl resins.

Examples of polyoxyalkylene glycols which can  
be used in combination with polyoxyethylene glycol  
15 include polyoxytetramethylene glycol, modified  
polyoxytetramethylene glycol and polyoxypropylene glycol  
which have a number average molecular weight of 500 -  
5,000, the proportion thereof in the glycol component  
being less than 50% by weight.

20 Said modified polyoxytetramethylene glycol may  
be products obtained by substituting a part of  
-(CH<sub>2</sub>)<sub>4</sub>-O- in usual polyoxytetramethylene glycol with  
-R-O-, wherein R is an alkylene group of 2-10 carbon  
atoms, e.g., the ethylene group, 1,2-propylene group,  
25 1,3-propylene group, 2-methyl-1,3-propylene group, 2,2-  
dimethyl-1,3-propylene group, pentamethylene group,  
hexamethylene group, etc. The amount of modification is  
not critical but is usually selected from the range of 3

1 - 50% by weight. Said amount of modification and the  
type of alkylene groups are appropriately selected  
depending on the properties required for the resulting  
vinyl resin compositions, e.g., low temperature impact  
5 resistance, thermal resistance, etc.

The modified polyoxytetramethylene glycol can  
be prepared, for example, by copolymerization of  
tetrahydrofuran with a diol using a heteropolyacid as  
the catalyst or copolymerization of a diol or a cyclic  
10 ether which is the condensation product of a diol, with  
butandiol.

The method for production of the  
polyamideimide elastomer used in the present composition  
is not particularly limited so long as it can produce a  
15 homogeneous amideimide elastomer. The following method  
may be used, for example.

This method comprises mixing caprolactam  
component (a), aromatic polycarboxylic acid component  
(b) and glycol component (c) in such a proportion that  
20 component (b) and component (c) are substantially  
equimolar, and polymerizing the mixture at 150 - 300°C,  
preferably 180 - 280°C, while maintaining the water  
content of the polymer formed at 0.1 - 1% by weight. In  
the dehydration condensation of this method, the  
25 reaction temperature may also be elevated stepwise.

In the reaction some of the caprolactam used  
remains unreacted, and is distilled off from the  
reaction mixture under reduced pressure. The reaction

1 mixture thus freed of unreacted caprolactam may be  
further polymerized, according to necessity, by being  
subjected to post-polymerization under reduced pressure  
at 200 - 300°C, preferably 230 - 280°C.

5 In the above-mentioned method of reaction,  
esterification and amidation are made to take place  
simultaneously during the course of dehydration  
condensation, whereby the separation of coarse phases is  
prevented and resulting in a homogeneous and transparent  
10 elastomer being formed. For this reason, the elastomer  
is excellent in compatibility with vinyl resins and,  
when blended with vinyl resins, exhibits an excellent  
antistatic effect and excellent mechanical properties,  
and further it can give a transparent composition with  
15 acrylic resins.

In order to make the reaction of  
esterification and the polymerization of caprolactam  
take place simultaneously and to control respective  
reaction velocities thereby to obtain transparent and  
20 homogeneous elastomers, it is preferable to perform the  
polymerization while maintaining the water content of  
the reaction system in the range of 0.1 - 1% by weight  
by removing water formed away from the reaction system.  
When the water content exceeds 1% by weight the polymer-  
25 ization of caprolactam takes place preferentially to  
cause coarse phase separation. When the content is less  
than 0.1% by weight, on the other hand, esterification  
takes place preferentially while the reaction of

1 caprolactam cannot proceed and consequently an elastomer  
of desired composition cannot be obtained. The water  
content is appropriately selected in the above-mentioned  
range according to the properties desired for the  
5 elastomer.

In the above reaction, the water content of  
the reaction system may be, as desired, also decreased  
gradually with the progress of the reaction. The  
control of the water content can be effected, for  
10 example, by the control of reaction conditions, e.g.,  
the reaction temperature, the flow rate of inert gas  
introduced, and the degree of pressure reduction, or the  
modification of the reactor structure.

Although the degree of polymerization of the  
15 polyamideimide elastomer used in the present composition  
may be varied as desired according to necessity, it is  
preferably selected so as to give a relative viscosity  
of at least 1.5 as determined at a concentration of 0.5%  
(weight/volume) in m-cresol at 30°C. When the viscosity  
20 is lower than 1.5 the elastomer cannot exhibit satis-  
factory mechanical properties and, also when blended  
with vinyl resins, often shows unsatisfactory mechanical  
properties. A preferable relative viscosity is at least  
1.6.

25 When a diamine or a diisocyanate (d) is used  
together, the reaction may be conducted by either a one  
step method or a two step method. The former method  
comprises simultaneously charging and reacting

1 caprolactam (a), polycarboxylic acid component (b),  
glycol component (c), and diamine or diisocyanate  
component (d). The latter method comprises first  
reacting polycarboxylic acid component (b) and diamine  
5 or diisocyanate component (d) and then adding  
caprolactam (a) and glycol component (c) thereto and  
reacting the resulting mixture.

In the production of the polyamideimide  
elastomer, an esterification catalyst may be used as a  
10 polymerization accelerator.

Examples of preferred polymerization  
accelerators include phosphorus compounds such as  
phosphoric acid, polyphosphoric acid, and metaphosphoric  
acid; tetraalkyl orthotitanates such as tetrabutyl  
15 orthotitanate; tetraalkoxyzirconium such as tetra-  
butylzirconium; tin-containing catalysts such as  
dibutyltin oxide and dibutyltin laurate; manganese-  
containing catalysts such as manganese acetate;  
antimony-containing catalysts such as antimony trioxide;  
20 lead-containing catalysts such as its acetate. The  
catalyst may be added at either the initial stage or the  
middle stage of polymerization.

Stabilizers including various thermal age  
resisters and antioxidants can be used to enhance the  
25 thermal stability of the polyamideimide elastomer  
obtained. These stabilizers may be added in any of the  
initial, middle and last stages of polymerization. They

1 may be added also after polymerization and before  
blending with vinyl resins.

Examples of heat stabilizers mentioned above  
include various hindered phenols such as N,N'-  
5 hexamethylenebis(3,5-di-t-butyl-4-hydroxycinnamamide),  
4,4'-bis(2,6-di-t-butylphenol), and 2,2'-methylenebis(4-  
ethyl-6-butylphenol); aromatic amines such as N,N'-  
bis( $\beta$ -naphthyl)-p-phenylenediamine N,N'-diphenyl-p-  
phenylenediamine, and poly(2,2,4-trimethyl-1,2-  
10 dihydroquinoline); copper salts such as copper chloride  
and copper iodide; sulfur compounds such as dilauryl  
thiodipropionate; phosphorus compounds, etc.

The ratio of the vinyl resin of component (A)  
to the polyamideimide elastomer of component (B) in the  
15 present composition should be in the range of 70:30 to  
97:3 by weight. When the ratio of component (B) is  
lower than said value a sufficient antistatic effect  
cannot be obtained, whereas when it is higher than the  
value the rigidity becomes insufficient.

20 It has been revealed that, in the present  
composition, a prominent synergistic effect is exhibited  
in antistatic effect when an electrolyte such as sodium  
dodecylbenzene sulfonate is used in combination with the  
polyamideimide elastomer.

25 Examples of organic electrolytes which show  
such an effect are organic compounds having an acidic  
group or the metal salts thereof, organic ammonium  
salts, or organic phosphonium salts, etc. Specific

1 examples of said organic compound having an acidic group  
or the metal salts thereof include aromatic sulfonic  
acids such as dodecylbenzenesulfonic acid, p-toluene-  
sulfonic acid, dodecyldiphenyl ether disulfonic acid,  
5 naphthalenesulfonic acid, condensation products of  
naphthalenesulfonic acid with formaline, and poly-  
styrenesulfonic acid; alkylsulfonic acids such as  
laurylsulfonic acid; organic carboxylic acids such as  
stearic acid, lauric acid and polyacrylic acid; organic  
10 phosphoric acids such as diphenyl phosphite and diphenyl  
phosphate; and the alkali metal salts and the alkaline  
earth metal salts thereof.

Although the organic electrolytes also exhibit  
their effect in the form of free acids, they are  
15 preferably used in the form of alkali metal salts or  
alkaline earth metal salts, for example sodium, lithium,  
potassium, magnesium and calcium salts.

Specific examples of organic ammonium salts  
are quaternary ammonium salts, such as trimethyloctyl-  
20 ammonium bromide, trimethyloctylammonium chloride,  
cetyltrimethylammonium bromide, cetyltrimethylammonium  
chloride, and trioctylmethylammonium bromide. Those of  
organic phosphonium salts are quaternary phosphonium  
salts, such as amyltriphenylphosphonium bromide and  
25 tetrabutylphosphonium bromide.

The inorganic electrolytes may be the  
nitrates, hydroxides, halides, rhodanates, sulfates,  
phosphates, carbonates, etc., of metals of the groups

1 Ia, Ib, IIa, IIb, VIIa and VIII. Specific examples thereof include  $\text{AgNO}_3$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{KBr}$ ,  $\text{KNCS}$ ,  $\text{KNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{LiCl}$ ,  $\text{NaBr}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{ZnSO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{MgCl}_2$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{MnCl}_2$  and  $\text{Ni}(\text{NO}_3)_2$ .

5 When styrene resin is used as the vinyl resin in the present composition, the electrolyte to be used can be selected as desired from those mentioned above depending on the composition of styrene resin and polyamideimide elastomer, intended uses, etc. When  
10 acrylic resin is used as the vinyl resin, organic sulfonic acid salts are preferably selected.

The amount of these electrolytes to be added is selected from the range of usually 0.01 - 10 parts by weight, preferably 0.1 - 5 parts by weight, relative to  
15 100 parts by weight of the sum of components (A) and (B). When the amount is less than 0.01 part by weight the effect of the additive is not exhibited sufficiently. When it exceeds 10 parts by weight, it causes lowering of impact strength, corrosion of molds,  
20 development of mold deposits, deterioration of appearance, etc.

Among the electrolytes mentioned above, organic electrolytes are preferred to inorganic electrolytes from the viewpoint of corrosion of molds  
25 and the appearance of products.

The composition of the present invention may be incorporated as desired, within limits not deleterious to the object of the present invention, with



1 various additive ingredients, for example pigments,  
dyes, reinforcing fillers, thermal stabilizers,  
antioxidants, nucleating agents, lubricants,  
plasticizers, ultraviolet absorbers, mold release  
5 agents, flame retardants, and other polymers, in any  
desired process steps such as the kneading step, molding  
step, etc.

As examples of the reinforcing filler, mention  
may be made of fibrous reinforcements such as glass  
10 fiber, carbon fiber and potassium titanate, and granular  
or flake-like fillers such as mica, talc, clay, calcium  
silicate, calcium carbonate, glass foil, glass beads,  
and other polymers. Particularly preferred among these  
are glass fiber and mica.

15 When flame resistance is to be imparted to the  
vinyl resin composition of the present invention, a  
flame retardant can be added thereto. Flame retardants  
which may be used include organic halogen-containing,  
organic phosphorus-containing, metal hydroxide-based  
20 flame-retardants etc., and those conventionally used in  
styrene resins.

The amount of said organic halogen-containing,  
organic phosphorus-containing or metal hydroxide-based  
flame retardants to be added to the vinyl resin  
25 composition is selected from the range of usually 4 - 35  
parts by weight, preferably 10 - 25 parts by weight,  
relative to 100 parts by weight of the vinyl resin  
composition.

1           Flame retarding auxiliaries which have the  
capability of enhancing the effect of the above-  
mentioned flame retardant can be used. Specific  
examples of the flame retarding auxiliary include  
5 molybdenum compounds such as molybdenum trioxide and  
ammonium molybdate, and antimony compounds such as  
antimony trioxide. Particularly preferred is antimony  
trioxide. The amount of the flame retarding auxiliary  
to be added is usually selected from the range of 2 - 10  
10 parts by weight relative to 100 parts by weight of the  
vinyl resin composition.

The composition of the present invention can  
be prepared from a mixture comprising said component  
(A), component (B), and optionally used electrolytes and  
15 various additives by conventional methods, for example  
by kneading the mixture with a Banbury mixer, mixing  
roll, single- or twin-screw extruder, etc. The kneading  
is preferably conducted at a temperature range of 180 -  
280°C.

20           For electrolytes which have a high melting  
point, it is advantageous to dissolve the electrolyte in  
a solvent, such as water, an alcohol and dimethyl-  
formamide, in advance and then feeding the resulting  
solution dropwise into the vent port of the extruder  
25 causing the electrolyte to thereby be dispersed  
uniformly and a composition which has good antistatic  
effect, mechanical properties and appearance can be  
obtained.

1           The vinyl resin composition thus obtained can  
be formed by known methods conventionally used in  
forming thermoplastic resins, for example, injection  
molding, extrusion, blow molding, vacuum forming, etc.

## 5   EFFECT OF THE INVENTION

          The vinyl resin composition of the present  
invention comprises styrene resin or acrylic resin and  
polyamideimide elastomer as essential resin components  
and is featured by having a permanent antistatic  
10   property and excellent mechanical properties. Accord-  
ingly, it is in wide use as a molding material capable  
of preventing electrostatic charge for various parts of  
electronic devices, household appliances, office automa-  
tion equipment etc., including video cassettes, video  
15   disks, cleaners, televisions, copying machines in the  
case of compositions based on styrene resins, and light-  
ing fixtures, meter covers, etc., in the case of those  
based on acrylic resins by virtue of their transparency.

## Example

20           The present invention will be described  
further in detail below with reference to Examples, but  
it is in no way limited thereto.

          The properties of the composition and the  
elastomer were determined according to the methods shown  
25   below.

- 1 (1) Tensile were determined according to ASTM D638 by  
use of dumbbell specimens of 1/8 inch thickness at 23°C  
and 55% RH.

Since many of the elastomers have no yield  
5 point, the tensile strength and elongation were  
determined by use of dumbbell specimens of 1 mm  
thickness at the absolute dry state.

(2) Flexural modulus:

This was determined according to ASTM D790 by  
10 use of test pieces of 1/8 inch thickness at 23°C and 55%  
RH.

(3) Izod impact strength:

This was determined according to ASTM D-256 by  
use of test pieces with notch of 1/8 inch thickness at  
15 23°C and 55% RH.

(4) Charge voltage test

A static voltage of 8 KV was applied to the  
specimen by use of a Static Honest Meter (mfd. by  
Shishido Shokai) and the time until the reduction by  
20 half of the charge voltage of the specimen after removal  
of the applied voltage was determined at 23°C and 55%  
RH.

(5) Surface resistivity

This was determined by use of plates of 1/8  
25 inch thickness with an Ultra Megohmmeter SM-10E (mfd. by  
Toa Denpa Kogyo K.K.) under the following conditions.

(a) Measured after conditioning at 23°C and  
55% RH for 24 hours, after molding.

1 (b) Measured after immersion in running water  
for 10 minutes, removal of surface water, and  
conditioning at 23°C and 55% RH for 24 hours, after  
molding.

5 (6) Relative viscosity of elastomer:

This was determined under conditions of 0.5%  
(wt/vol) in m-cresol at 30°C.

(7) Thermal decomposition temperature of elastomer:

The temperature at which the specimen shows a  
10 specified weight decrease was determined by differential  
thermal analysis at a temperature-increasing rate of  
10°C/min.

Test pieces used for determination of  
properties were prepared by molding the pellets obtained  
15 in Examples and Comparative Examples into plates of 1/8  
inch thickness (90 mm in length and 50 mm in width) and  
test pieces of 1/8 inch thickness with an injection  
machine.

The following styrene resins, acrylic resins  
20 and additives were used in Examples and Comparative  
Examples.

A-1: A styrene resin containing 12% by weight of  
butadiene rubber

A-2: A styrene resin (having a melt flow rate of  
25 2.3 g/10 mm as determined at 200°C and 5 kg)

A-3: A styrene resin containing 8% by weight of  
methacrylic acid copolymerized therein.

- 1 A-4: An ABS resin, Stylac ABS A-4130 (mfd. by Asahi Chemical Industry Co., Ltd.)
- A-5: An AS resin, Stylac AS (mfd. by Asahi Chemical Industry Co., Ltd.)
- 5 A-6: A styrene-methyl methacrylate-methacrylic acid (60:30:10) copolymer
- A-7: A polystyrene resin containing 1% by weight of oxazoline groups (XUS-40056-01, mfd. by Dow Chemical Co.)
- 10 A-8: A polystyrene resin containing 15% by weight of 2-hydroxyethyl methacrylate copolymerized therein
- A-9: A polymethyl methacrylate containing 5% by weight of glycidyl methacrylate copolymerized therein
- A-10: A methyl methacrylate resin, Delpet 8 ON (mfd. by Asahi Chemical Industry Co., Ltd.)
- 15 A-11: A copolymer resin of 90 parts by weight of methyl methacrylate and 10 parts by weight of methacrylic acid
- A-12: A copolymer resin of 70 parts by weight of methyl methacrylate, 15 parts by weight of styrene and 15 parts by weight of acrylonitrile
- 20 A-13: A copolymer resin of 85 parts by weight of methyl methacrylate and 15 parts by weight of ethyl acrylate
- 25 C-1: Sodium dodecylbenzenesulfonate
- C-2: Sodium dodecyl diphenyl ether-disulfonate
- C-3: Sodium dodecyl diphenyl ether-disulfonate
- C-3: Potassium bromide

- 1 C-4: Potassium thiocyanate
- C-5: Sodium stearate
- C-6: Amylphenylphosphonium bromide
- C-7: Tetrabutylammonium chloride
- 5 C-8: Sodium polyacrylate
- C-9: Sodium laurylsulfate

Preparation Example 1: Preparation of polyamideimide elastomer (B-1)

In a 10 l SUS reactor equipped with a stirrer, 10 nitrogen inlet and distilling-out tube were placed 2,680 g of polyoxyethylene glycol (number average molecular weight: 1,980), 259.4 g of trimellitic anhydride, 1,707 g of caprolactam and 8.0 g of a 1:1 blend of penta-  
15 erythrityl-tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate] with tris(2,4-di-t-butylphenyl)phosphite (Irganox B 225, a trade name, an antioxidant), then the inner pressure was reduced to 1 Torr at 100°C, and the above mixture was stirred for 1 hour to remove the moisture in the raw materials. Thereafter, while  
20 introducing nitrogen and maintaining the inner pressure at 300 Torr, the mixture was heated at 260°C and polymerized for 4 hours. Then, the pressure was gradually reduced at the same temperature to distill off unreacted caprolactam.

25 Subsequently, nitrogen was again introduced to keep the pressure at 200 Torr, a solution of 4.0 g of tetrabutyl orthotitanate in 100 g of caprolactam was

1 added to the above polymerization mixture, then the  
pressure was reduced to 1 Torr, and polymerization was  
conducted at the same temperature for 7 hours. The  
polymer thus obtained was extruded in the form of gut  
5 onto a cooling belt and pelletized to give a pellet-  
formed elastomer.

The elastomer was pale brown and transparent,  
had a polyoxyethylene glycol content of 67% by weight  
and a relative viscosity of 2.18, and showed a tensile  
10 strength and elongation of 310 kg/cm<sup>2</sup> and 850%,  
respectively.

The thermal decomposition initiation  
temperature, 10% weight decrease temperature and 30%  
weight decrease temperature of the elastomer were 353°C,  
15 377°C and 394°C, respectively.

#### Preparation Example 2: Preparation of polyamideimide elastomer (B-2)

In a 50 ml separable flask equipped with a  
stirrer, nitrogen inlet and distilling-out tube were  
20 placed 144 g of polyoxyethyleneglycol (number average  
molecular weight: 2,010), 13.7 g of trimellitic  
anhydride, 68.2 g of caprolactam and 0.4 g of  
poly(2,2,4-trimethyl-1,2-dihydroquinoline) (Noclac 224,  
a trade name, an antioxidant), and the resulting mixture  
25 was removed of water by reducing the inner pressure to 1  
Torr or less for 30 minutes while stirring the mixture  
at 100°C. Then the pressure was returned to normal



1 pressure, and the mixture was heated to 260°C while  
nitrogen was being passed through the reactor at a rate  
of 60 ml/minute and polymerized for 4 hours. Thereafter  
the pressure was reduced gradually at the same  
5 temperature to distill unreacted caprolactam out of the  
reaction system.

Then 0.4 g of tetrabutyl orthotitanate was  
added to the system, the pressure was reduced to 1 Torr,  
and polymerization was conducted for 7 hours to obtain a  
10 pale yellow, transparent elastomer.

The elastomer had a content of polyoxyethylene  
glycol of 72% by weight, a number average molecular  
weight of polyamideimide of 80 and a relative viscosity  
of 2.25, and showed a tensile strength and elongation of  
15 290 kg/cm<sup>2</sup> and 1,200%, respectively.

The thermal decomposition initiation  
temperature, 10% weight decrease temperature and 30%  
weight decrease temperature were 350°C, 425°C and 443°C,  
respectively.

20 The water contents in the polymerization  
system 1, 2 and 4 hours after the initiation of reaction  
at 26-°C were 0.7% by weight, 0.6% by weight and 0.6% by  
weight, respectively.

Preparation Examples 3-8: Preparation of polyamideimide  
25 elastomers (B-3 to B-7) and polyamide elastomer (B-8)

1 Polyamideimide elastomers and a polyamide  
elastomer having compositions shown in Table 1 were  
prepared in the same manner as in Preparation Example 2.

In Preparation Example 5, tetrabutoxyzirconium  
5 was used in place of tetrabutyl orthotitanate. In  
Preparation Example 7, 0.1% by weight of antimony  
trioxide was charged to effect reaction and, after  
distilling caprolactam off, polymerization was conducted  
by use of 0.1% by weight of tetrabutyl orthotitanate.  
10 In Preparation Example 6, polyoxytetramethylene glycol  
(PTMG) was used as a part of the glycol component.

The neopentyl glycol-modified polyoxytetra-  
methylene glycol (abbreviated as NPG-modified PTMG) used  
in Preparation Example 7 was prepared in the following  
15 manner.

In a vessel equipped with a stirrer and reflux  
condenser were placed 600 g of tetrahydrofuran (THF) and  
70.5 g of neopentyl glycol and 300 g of anhydrous  
tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ), which was heated at  
20 250°C for 3 hours. After 7 hours of stirring at a  
temperature of 60°C under nitrogen, the reaction mixture  
was allowed to stand at room temperature to separate  
into two layers. Unreacted THF was removed by  
distillation from the upper layer to obtain 142 g of a  
25 transparent viscous polymer.

Determination of the hydroxyl group showed  
that the polymer had a number average molecular weight

1 of 1,060 and was a copolymer glycol of a molar ratio of THF: neopentyl glycol of 5:1.

The results thus obtained are shown in Tables 1 and 2 below.

Table 1

Prepara- tion Example No.	Elasto- mer	Glycol component I	Glycol component II	I/II weight ratio	Carboxylic acid	Glycol content (wt%)
3	B-3	PEG Mn 1480	-	-	Trimellitic acid	60
4	B-4	PEG Mn 1000	-	-	Trimellitic anhydride	50
5	B-5	PEG Mn 1980	-	-	Pyromellitic anhydride	73
6	B-6	PEG Mn 1980	PTMG Mn 1980	70/30	Trimellitic anhydride	67
7	B-7	PEG Mn 1980	NPG-modified PTMG Mn 1970	80/20	Benzophenone- tetracarboxylic acid anhydride	58
8	B-8	PTMG Mn 1980	-	-	Adipic acid	67

Table 2

Elasto- mer	Relative viscosity	Strength (kg/cm <sup>2</sup> )	Elongation (%)	Thermal decomposition temp. (°C)	10% Weight decrease temp. (°C)	30% Weight decrease temp. (°C)
B-3	1.84	280	1050	366	387	407
B-4	2.04	560	900	350	385	405
B-5	1.93	275	1080	336	436	452
B-6	2.09	315	980	340	385	418
B-7	1.81	330	890	331	382	410
B-8	1.97	345	930	283	374	403

1 Preparation Example 9: Preparation of polyamide  
elastomer (B-9)

In the same apparatus as that used in  
Preparation Example 2 except that the distilling-out  
5 tube was replaced by a reflux condenser, were placed 167  
g of caprolactam, 33.2 g of adipic acid and 6 g of water  
and reacted at 260°C for 6 hours to obtain a carboxyl  
group-terminated polycapramide. The number average  
molecular weight of the polycapramide was found to be  
10 883 from the acid value determination.

In the same apparatus as that used in  
Preparation Example 2, were placed 40 g of the polyamide  
mentioned above, 96 g of polyoxyethylene glycol (number  
average molecular weight: 2,010), 0.3 g of an  
15 antioxidant [N,N-hexamethylene-bis(3,5-di-t-butyl-4-  
hydroxycinnamamide), trade name: Irganox 1,098] and 0.2  
g of tetrabutyl orthotitanate, the resulting mixture was  
molten at 240°C and then polymerized at a reduced  
pressure of 1 Torr at the temperature for 2 hours and  
20 further at 1 Torr and 260°C for 9 hours. Resultantly,  
coarse phase separation occurred during polymerization.

The molten mixture assumed a milky white  
appearance and did not become transparent to the end of  
polymerization. The elastomer obtained was polar brown,  
25 opaque and brittle.

The thermal decomposition initiation  
temperature, 10% weight decrease temperature and 30%

- 1 weight decreased temperature of the elastomer were  
291°C, 362°C and 380°C, respectively.

Preparation Example 10: Preparation of polyamideimide  
elastomer (B-10)

- 5 In the same apparatus as that used in  
Preparation Example 2, were placed 40 g of caprolactam,  
91 g of polyoxyethylene glycol (number average molecular  
weight: 2,040), 11.2 g of trimellitic anhydride, 1.5 g  
of hexamethylenediamine (molar ratio to polyoxyethylene  
10 glycol: 0.3), 0.15 g of phosphoric acid and 0.2 g  
of "Noclac 224", and the resulting mixture was allowed  
to react at 260°C for 4 hours while nitrogen was being  
passed through the reactor at a rate of 70 l/min. Then  
unreacted caprolactam was distilled off under reduced  
15 pressure, 0.3 g of tetraisopropyl orthotitanate was  
added to the reaction mixture, and the resulting mixture  
was reacted at 1 Torr for 5 hours to obtain a yellow  
transparent elastomer.

- The elastomer had a polyoxyethylene glycol  
20 content of 72% by weight, relative viscosity of 1.90,  
tensile strength of 295 kg/cm<sup>2</sup> and tensile elongation of  
1,020%. It showed a thermal decomposition initiation  
temperature, 10% weight decreases temperature and 30%  
weight decrease temperature of 350°C, 403°C and 438°C,  
25 respectively.

1 Preparation Example 11: Preparation of polyamideimide elastomer (B-11)

In the same apparatus as that used in Preparation Example 2, were placed 95 g of caprolactam, 5 82.5 g of polyoxyethylene glycol having a number average molecular weight of 1,980, 8.8 g of trimellitic anhydride, 1.04 g of diphenylmethane diisocyanate and 0.3 g of "Irganox 1098", and the resulting mixture was molten at 150°C while nitrogen was being passed at a 10 rate of 50 ml/min. and then polymerized at 260°C for 4 hours. Subsequently, 0.3 g of tetrabutyl orthotitanate was added, and then the pressure was gradually reduced down to 1 Torr to distill unreacted caprolactam out of the system. Polymerization was further conducted at the 15 same temperature under a pressure of 1 Torr or less for 3 hours to obtain a transparent elastomer. The elastomer had a polyoxyethylene glycol content of 55% by weight, relative viscosity of 2.0, tensile strength of 380 kg/cm<sup>2</sup>, elongation of 920%, and Shore hardness D of 34. 20 It showed a thermal decomposition initiation temperature, 10% weight decrease temperature and 30% weight decrease temperature of 321°C, 380°C and 405°C, respectively.

Preparation Example 12: Preparation of polyamideimide 25 elastomer (B-12)

Reaction was conducted in the same manner as in Preparation Example 10 by use of 90 g of



polyoxyethylene glycol having a number average molecular weight of 1,490, 67.4 g of caprolactam, 13.9 g of trimellitic anhydride and 2.0 g of hexamethylene diisocyanate to obtain a transparent elastomer having a polyoxyethylene glycol content of 60% by weight, relative viscosity of 1.95, tensile strength and elongation of 290 kg/cm<sup>2</sup> and 1,030%, respectively, and Shore hardness D of 27. The thermal decomposition initiation temperature, 10% weight decrease temperature and 30% weight decrease temperature of the elastomer were 335°C, 392°C and 415°C, respectively.

Preparation Example 13: Preparation of polyamideimide elastomer (B-13)

In the same reactor as that used in Preparation Example 1 were placed 1.45 kg of caprolactam, 2.0 kg of polyoxyethylene glycol having a number average molecular weight of 1,480, 259 g of trimellitic anhydride and 7 g of "Noclac 224", and the same procedures as in Preparation Example 1 were followed except that the fore stage reaction was conducted at 600 Torr, to obtain a transparent polyamideimide elastomer containing 60% by weight of polyoxyethylene glycol. The elastomer obtained had a relative viscosity of 2.15, tensile strength of 325 kg/cm<sup>2</sup> and elongation of 980%, and showed a thermal decomposition initiation temperature of 359°C, 10%

- 1 weight decrease temperature of 390°C and 30% weight  
decrease temperaturer of 409°C.

#### Examples 1-18

- 5 Styrene resins, elastomers and additives were  
mixed in the proportions shown in Table 3, kneaded and  
extruded through a single screw extruder (30 mm screw  
with dulmadge, L/D=26) at 240°C, then passed through a  
cooling bath and pelletized. The pellets thus obtained  
10 were dried in a Geer over at 80°C for 3 hours and then  
injection-molded under the following conditions to  
prepare test pieces for property determination. All the  
test pieces showed excellent gloss.

- |    |                       |                        |
|----|-----------------------|------------------------|
|    | Cylinder temperature: | 250°C                  |
|    | Mold temperature:     | 80°C                   |
| 15 | Injection pressure:   | 700 kg/cm <sup>2</sup> |
|    | Injection time:       | 15 sec.                |
|    | Cooling time:         | 15 sec.                |

The results of property determination are  
shown in Table 3.

#### 20 Comparative Examples 1-4

- Styrene resins, or styrene resins and  
elastomers, were blended in the proportions shown in  
Table 3, and the properties of the blends were  
determined in the same manner as in Examples 1-18. The  
25 results are shown in Table 3 below.

Table 3

	Composition of resin composition						Additive	
	Elastomer		Vinyl resin				Kind	Part by wt.
	Name	Part by wt.	X	Y	Z	Part by wt. X/Y/Z		
Example	B-1	10	A-1	A-2	-	45/45/0	-	0
	B-1	8	A-1	A-2	A-3	46/34.4/11.6	-	0
	B-1	8	A-1	A-2	A-3	46/34.4/11.6	C-1	1.0
	B-2	6	A-1	A-2	-	47/47/0	-	0
	B-3	20	A-1	-	A-3	40/0/40	-	0
	B-4	10	A-1	A-2	-	60/30/0	C-2	0.5
	B-5	10	A-1	A-2	A-3	45/33.7/11.3	C-3	0.5
	B-6	10	A-1	A-2	A-3	45/33.7/11.3	C-4	0.3
	B-7	12	A-1	A-2	-	44/44	-	-
	B-10	12	A-1	A-7	-	44/44	C-6	1.0
	B-10	10	A-1	A-2	A-3	45/33.7/11.3	C-8	1.0
	B-11	10	A-1	A-2	A-3	45/33.7/11.3	C-1	0.5
	B-12	10	A-1	A-2	A-3	45/33.7/11.3	C-5	0.5
	B-11	10	A-1	A-2	A-9	54/27/9	C-7	1.0
	B-11	15	A-1	A-2	-	50/35/0	C-2	0.2
	B-1	10	A-1	A-2	A-8	45/35/10	C-1	0.3
	B-1	18	A-4	-	-	82/0/0	-	0
	B-3	12	A-5	-	A-6	70.4/0/17.6	-	0
Comp. Example	-	-	A-1	A-2	-	50/50/0	-	0
	1	-	A-1	A-2	A-3	50/37.5/12.5	-	0
	2	-	A-1	A-2	A-3	45/33.7/11.3	-	0
	3	10	A-1	A-2	A-3	45/33.7/11.3	-	0
	4	10	A-1	A-2	A-3	45/33.7/11.3	-	0

- Cont'd -

Table 3 (Cont'd)

Property of resin composition				
Withstand voltage test (sec)	Izod impact strength (kg·cm/cm)	Flexural modulus (kg/cm <sup>2</sup> )	Strength (kg/cm <sup>2</sup> )	Appearance
2	9.5	23000	360	Glossy, good
10	11.5	23300	365	"
2	11.0	23200	360	"
27	9.7	24300	362	"
4	11.7	19500	325	"
2	14.2	21600	350	"
2	8.3	19500	310	"
2	10.3	21200	345	"
4	10.1	22300	350	"
2	9.6	22100	305	"
2	9.5	21000	310	"
2	10.9	22500	355	"
3	10.2	22300	350	"
3	13.8	21200	345	"
2	12.1	20800	335	"
3	10.1	23100	310	"
2	43	17500	320	"
10	3.5	29500	620	"
>3000	10.3	27600	377	"
>3000	9.6	26400	381	"
740	10.1	18200	290	"
35	2.3	21300	315	Slightly poor gloss

## 1 Examples 19-25

Acrylic resins, elastomers and additives were mixed in the proportions shown in Table 4, kneaded and extruded through a single screw extruder (30 mm screw  
5 with dulmadge, L/D=26) at 250°C, then passed through a cooling bath and pelletized. The pellets obtained were dried in a Geer oven at 80°C for 3 hours and then injection-molded under the following conditions to prepare test pieces for property determination. All the  
10 test pieces showed excellent gloss.

Cylinder temperature: 250°C

Mold temperature: 80°C

Injection pressure: 700 kg/cm<sup>2</sup>

Injection time: 15 sec.

15 Cooling time: 15 sec.

The results of property determination are shown in Table 4.

## Comparative Examples 5-8

Acrylic resins, or acrylic resins and  
20 elastomers, were blended in the proportions shown in Table 4, and the properties of the blends were determined in the same manner as in Examples 19-25. The results of property determination are shown in Table 4.

Table 4

	Resin composition							Additive	
	Elastomer		Acrylic resin					Kind	Part by wt.
			First component		Second component				
	Kind	Part by wt.	Kind	Part by wt.	Kind	Part by wt.			
19			B-1	20	A-10	80	-	-	-
Example	20	B-2	15	A-10	85	-	-	-	
	21	B-2	8	A-10	92	-	-	C-1	1.0
	22	B-3	10	A-10	70	A-11	20	C-9	1.0
	23	B-4	10	A-10	90	-	-	C-2	1.0
	24	B-6	20	A-10	50	A-12	30	-	-
	25	B-1	10	A-13	90	-	-	C-1	0.5
	5	-	-	A-10	100	-	-	-	-
	6	-	-	A-10	100	-	-	C-1	1.0
Comparative Example	7	B-8	20	A-10	80	-	-	-	-
	8	-	-	A-10	88	A-11	12	-	-

- Cont'd -

Table 4 (Cont'd)

Withstand voltage test (sec)	Property			Appearance
	Flexural modulus (kg/cm <sup>2</sup> )	Strength (kg/cm <sup>2</sup> )	Elongation (%)	
3	24100	490	82	Transparent
20	28200	520	50	Transparent
3	30200	635	44	Transparent
5	29000	530	53	Translucent
4	30400	630	47	"
12	24800	500	32	Transparent
3	27800	535	47	Transparent
>3000	34100	770	9	Transparent
>3000	33000	735	8	Transparent
>3000	24500	510	60	Translucent
>3000	33800	750	10	Transparent

## 1 Example 26

The surface resistivities of the test pieces of Examples 1 and 3 were determined at 23°C and 55% RH and found to be  $4.3 \times 10^{11} \Omega/\square$  and  $2.5 \times 10^{11} \Omega/\square$ ,  
5 respectively. The surface resistivities determined after standing under said conditions for 6 months were respectively  $4.1 \times 10^{11} \Omega/\square$  and  $2.8 \times 10^{11} \Omega/\square$ , showing that the initial values were maintained.

## Example 27

10 To a mixture of 10 parts by weight of the elastomer of Preparation Example 13 with respectively 45, 33.7, and 1.3 parts of styrene resins A-1, A-2 and A-3 was added 1 part by weight of sodium dodecylbenzene-sulfonate per 100 parts by weight of the sum of  
15 elastomer and styrene resin, and the resulting mixture was kneaded under the same conditions as in Example 1 to obtain a resin composition, which was then injection-molded under the same conditions as in Example 1. The sample thus obtained showed a surface resistivity of 5.0  
20  $\times 10^{11} \Omega/\square$  and a gloss of 90%.

To examine the thermal stability in injection molding, the resin composition was injection-molded after retention of 20 minutes at 250°C in the cylinder. The surface of the molded piece was smooth and had a  
25 gloss of 87%, thus showing substantially no change.

For comparison, the resin composition of Comparative Example 4 was injection-molded in the same



1 manner as in Example 1 at 250°C and, separately, after  
retention of 20 minutes in the cylinder at 250°C. The  
test pieces thus obtained showed a gloss of 73% and 37%,  
respectively. The latter test piece somewhat developed  
5 surface roughness.

#### Example 28

The test piece prepared in Example 3 was  
immersed in running water for 1 day, then dried in vacuo  
at 80°C and subjected to a withstand voltage test. The  
10 half value period of withstand voltage was found to be 3  
sec, which was the same as that before water-washing.

#### Example 29

Injection-molded samples of Examples 19 and 21  
were allowed to stand at 23°C and 55% RH for 2 months  
15 and then subjected to a withstand voltage test. Both  
samples gave a value of 3 sec., thus showing no change.  
Separately, the samples allowed to stand for 2 months  
were wiped 20 times with cloth and subjected to a  
withstand voltage test. Both samples gave a value of 3  
20 sec., thus showing no change.

#### Comparative Example 9

Twenty (20) parts by weight of a polyamide  
elastomer (B-9, polyoxyethylene glycol segment content:  
69.5% by weight) and 80 parts by weight of an acrylic  
25 resin (A-1) were blended and injection-molded in the

1 same manner as in Example 19. The injection-molded  
product gave a value of 3 sec. in the withstand voltage  
test but it was opaque and showed a low Izod impact  
strength of 1 kg.cm/cm. The Izod impact strength in  
5 Example 19 was 3 kg.cm/cm.

#### Example 30

To the composition of Example 21 were further  
added two kinds of ultraviolet absorbers, namely 0.1% by  
weight of 2-(5-methyl-2-hydroxyphenyl)benzotriazole  
10 (trade name: TINUVIN P, mfd. by Ciba Geigy Corp.) and  
0.2% by weight of bis-[2,2,6,6-tetramethyl-4-  
piperidinyl] sebacate (trade name: SANOL LS-770, mfd. by  
Sankyo K.K.) and the resulting mixture was kneaded and  
injection-molded under the same conditions as in Example  
15 21 to obtain a transparent test sample. The sample was  
subjected to a Sunshine weather meter test (continuous  
irradiation of repeated cycles each consisting of 48  
minutes of irradiation at 40°C and 72% RH and 12 minutes  
of irradiation under water spray) for 500 hours. The  
20 sample after irradiation maintained its transparency and  
showed only a little increase in yellowish color. The  
results of the withstand voltage test were 3 sec. before  
irradiation and 4 sec. after irradiation, thus showing  
almost no change in antistatic effect.

## 1 INDUSTRIAL APPLICABILITY

The vinyl resin composition according to the present invention has an excellent permanent antistatic property and can be used for parts of various electronic goods such as various office automation equipment and household appliances wherein prevention of electrostatic charge is required. In particular, when the composition is that based on acrylic resin, it can be also widely used for such uses as lighting fixtures, instrument nameplates, meter covers, etc. because it is inexpensive and excellent in transparency. When the composition is that based on styrene resins it is highly applicable also for video cassettes, IC cards, etc. because it is inexpensive and excellent in mechanical properties including mechanical strength and rigidity and in moldability.

## THE CLAIMS

1. A vinyl resin composition which comprises 100 parts by weight of a resin composition comprising
  - (A) 97-70% by weight of a vinyl polymer and
  - (B) 3-30% by weight of a polyamideimide elastomer obtained by reacting
    - a) caprolactam,
    - b) a tribasic or tetrabasic aromatic polycarboxylic acid capable of forming at least one imide ring,
    - c) polyoxyethylene glycol or a mixture of at least 50% by weight of polyoxyethylene glycol and a polyoxyalkylene glycol other than polyoxyethylene glycol, and
    - d) 0 - 0.5 mole of a diamine or diisocyanate compound per 1 mole of the glycol of component c), glycol component c) being present in a proportion of 85-30% by weight in the elastomer and the relative viscosity of said elastomer being at least 1.5 at a temperature of 30°C, and
  - (C) 0-10 parts by weight of at least one electrolyte selected from organic electrolytes and inorganic electrolytes.
2. A vinyl resin composition according to claim 1 characterized in that vinyl polymer (A) is a styrene resin.

3. A vinyl resin composition according to claim 1 characterized in that vinyl resin (A) is an acrylic resin.

4. An acrylic resin composition according to claim 3 wherein the polyamideimide elastomer contains 85-65% by weight of polyoxyethylene glycol and the composition is transparent.

5. A vinyl resin composition according to claim 1, 2 or 3 wherein the electrolyte is the alkali metal salt of an aromatic sulfonic acid or alkylsulfonic acid and the amount thereof is 0.1-5 parts by weight.

6. A vinyl resin composition according to claim 1, 2, 3 or 5 wherein hexamethylene diisocyanate or 4,4'-diphenylmethane diisocyanate is used as the diisocyanate compound.

7. A vinyl resin composition according to claim 1, 2, 3 or 5 wherein hexamethylene-diamine or 4,4'-diphenylmethanediamine is used as the diamine compound.

8. A vinyl resin composition according to claim 4, 6 or 7 wherein trimellitic anhydride or trimellitic acid is used as the aromatic polycarboxylic acid.

# INTERNATIONAL SEARCH REPORT

International Application No PCT/JP89/01329

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup> According to International Patent Classification (IPC) or to both National Classification and IPC  <div style="display: flex; justify-content: space-around; font-family: monospace; font-size: 1.2em;"> <span>Int. Cl<sup>5</sup></span> <span>C08L25/00</span> </div>											
<b>II. FIELDS SEARCHED</b>  <div style="text-align: center; font-size: 0.8em;">Minimum Documentation Searched <sup>7</sup></div> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; font-size: 0.8em;">Classification System</th> <th style="font-size: 0.8em;">Classification Symbols</th> </tr> <tr> <td style="text-align: center; padding: 10px;">IPC</td> <td style="padding: 10px;">C08L25/00 - 25/14, C08L101/00 - 101/08</td> </tr> </table> <div style="text-align: center; font-size: 0.8em; margin-top: 5px;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup></div>			Classification System	Classification Symbols	IPC	C08L25/00 - 25/14, C08L101/00 - 101/08					
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IPC	C08L25/00 - 25/14, C08L101/00 - 101/08										
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> Jitsuyo Shinan Koho  Kokai Jitsuyo Shinan Koho </div> <div style="width: 50%;"> 1947 - 1989  1973 - 1989 </div> </div>											
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; font-size: 0.8em;">Category <sup>10</sup></th> <th style="font-size: 0.8em;">Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup></th> <th style="width: 15%; font-size: 0.8em;">Relevant to Claim No. <sup>13</sup></th> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">JP, A, 62-116659 (General Electric Co.), 28 May 1987 (28. 05. 87), &amp; US, A, 4639486 &amp; EP, A, 219014</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1 - 8</td> </tr> <tr> <td style="text-align: center; vertical-align: top; padding: 5px;">X</td> <td style="padding: 5px;">JP, A, 58-134135 (Japan Synthetic Rubber Co., Ltd.), 10 August 1983 (10. 08. 83), (Family: none)</td> <td style="text-align: center; vertical-align: top; padding: 5px;">1 - 8</td> </tr> </table>			Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>	X	JP, A, 62-116659 (General Electric Co.), 28 May 1987 (28. 05. 87), & US, A, 4639486 & EP, A, 219014	1 - 8	X	JP, A, 58-134135 (Japan Synthetic Rubber Co., Ltd.), 10 August 1983 (10. 08. 83), (Family: none)	1 - 8
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<div style="display: flex; justify-content: space-between; font-size: 0.8em;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"F" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>											
<b>IV. CERTIFICATION</b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; padding: 5px;"> Date of the Actual Completion of the International Search   <div style="font-family: monospace; font-size: 1.1em;">March 26, 1990 (26. 03. 90)</div> </td> <td style="width: 50%; padding: 5px;"> Date of Mailing of this International Search Report   <div style="font-family: monospace; font-size: 1.1em;">April 9, 1990 (09. 04. 90)</div> </td> </tr> <tr> <td style="padding: 5px;"> International Searching Authority   <div style="font-family: monospace; font-size: 1.1em;">Japanese Patent Office</div> </td> <td style="padding: 5px;"> Signature of Authorized Officer   </td> </tr> </table>			Date of the Actual Completion of the International Search  <div style="font-family: monospace; font-size: 1.1em;">March 26, 1990 (26. 03. 90)</div>	Date of Mailing of this International Search Report  <div style="font-family: monospace; font-size: 1.1em;">April 9, 1990 (09. 04. 90)</div>	International Searching Authority  <div style="font-family: monospace; font-size: 1.1em;">Japanese Patent Office</div>	Signature of Authorized Officer  					
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